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Title: Magnesia-Calcia-Based Refractory

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SPECIFICATION

Title of the Invention

Magnesia-calcia-based refractory

Claims

(1) A magnesia-calcia-based refractory that contains 100 parts by weight of a refractory aggregate composed of 20-95% by weight of MgO and 80-5% by weight of CaO and 0.5-5 parts by weight of aragonite-type calcium carbonate with a particle diameter of 0.5-10 mm.

Detailed Explanation of the Invention

Industrial field of utilization

The present invention relates to a magnesia-calcia-based refractory with excellent spalling resistance.

Prior art and problems therein

Dolomite-based refractories have been widely used as the lining for various types of furnaces such as rotary furnaces, basic steelmaking furnaces, and cement rotary kilns. The appearance of refractories with better spalling resistance, thermal impact resistance, and the like has been demanded recently, however, as more rigorous operating conditions such as larger furnace size, higher tapping temperature, and shorter blow time have come to be used.

Basic refractories made mainly of magnesia (referred to hereinafter as MgO) have been developed in response to this situation. Although these refractories have excellent resistance to melting loss by highly basic slag, their major drawback is their inferior spalling resistance. Specifically, since the reactivity between MgO and slag is low, the slag penetrates to the interior of the brick that has a temperature corresponding to the melting point of the [illegible] slag and loosens the crystal structure of the MgO crystals (periclase) present in the part penetrated. Physical differences (such as in thermal swelling coefficient, porosity, and strength) develop as a result between the parts penetrated and the parts not penetrated when the temperature of the brick drops and spalling tends to occur. Also, since MgO has a high thermal swelling coefficient, spalling also tends to occur due to differences in the swelling of the side of the brick to the inside of the furnace

(high-temperature side) and the back side (low-temperature side). Therefore, thermal spalling and structural spalling develop in the brick due to a combination of various factors such as the action of the slag, heat warping caused by the construction of the furnace body, and the use cycle of the furnace (repeated heating and cooling) in MgO-based brick. The brick gradually detaches from the furnace body and the furnace eventually becomes unusable.

MgO-calcia (CaO)-based refractory brick that combines zirconia (more preferably stabilized zirconia) has been devised to resolve the aforementioned drawbacks of MgO-based brick (see Japanese Kokai Patent No. Sho 49-96003). In this brick, the slag that has penetrated to the interior of the brick and the zirconia react near the surface of the brick, thereby raising the viscosity of the slag. This is said to prevent further penetration of the slag and to improve the structural spalling resistance. However, this refractory brick offers almost no improvement of the thermal spalling resistance.

MgO-CaO-based refractories that combine raw materials such as dolomite and CaO with an MgO raw material have also been developed and are used frequently. Such refractories have high strength, but inadequate spalling resistance, thermal impact resistance, and the like. When used as a lining material for cement rotary kilns and such in particular, a coating layer made from cement components is usually formed on the surface of the refractory near the calcining zone and can be expected to lengthen the life of the refractory. In actuality, however, the coating layer is repeatedly desorbed violently by the rotation of the kiln and such, exposing the refractory surface to severe thermal impact and leading to spalling.

<u>Problems to be resolved by the invention</u>

The present inventors discovered as a result of various studies conducted in view of the present state of the technology as described above that the spalling resistance, thermal impact resistance, and the like can be improved without harming the inherently excellent properties (such as high strength) of MgO-CaO-based refractories by combining a specific proportion of aragonite-type calcium carbonate of a specific particle diameter with the MgO-CaO-based refractory material.

Specifically, the present invention relates to a magnesia-calcia-based refractory that contains 100 parts by weight of a refractory aggregate composed of 20-95% by weight of MgO and 80-5%

by weight of CaO and 0.5-5 parts by weight of aragonite-type calcium carbonate with a particle diameter of 0.5-10 mm.

Known basic refractory materials that contain MgO and/or CaO can be used as the refractory aggregate employed in the present invention. Concrete examples include magnesia clinker, dolomite clinker, and lime clinker. Magnesia clinker includes natural magnesia clinker, seawater magnesia clinker, and electrolyzed magnesia clinker. Dolomite clinker includes natural dolomite clinker, synthetic dolomite clinker, and electrolyzed dolomite clinker. The proportions are adjusted to 20-95% by weight of MgO (simply referred to hereinafter as %) and 80-5% of CaO by using one or two or more types of these in the present invention. The slaking resistance becomes inadequate and the slag melting loss resistance drops when the MgO is less than 20%. On the other hand, the spalling resistance and resistance to slag penetration decrease when the MgO exceeds 95%. The particle diameter of the refractory aggregate is usually about 10 mm or less, more preferably 3 mm or less.

Any known one can be used as the aragonite-type calcium carbonate employed in the present invention. Two or more types may also be used in mixture if necessary. When the raw material mixture is used during manufacture of the refractory of the present invention, the aragonite-type calcium carbonate changes into calcite type during calcining at 330-480°C. This is associated with sudden volumetric swelling. A large number of microcracks consequently develop in the brick. According to research conducted by the present inventors, these microcracks actualize a preventative effect against stress propagation during use and are very effective in preventing the expansion of cracks caused by thermal spalling. This remarkable effect in the present invention is obtained only when aragonite-type calcium carbonate is used. Specifically, when refined calcium carbonate (calcite-type $CaCO_3$) was used instead of aragonite-type calcium carbonate, spherical spaces that had no preventative effect against crack expansion formed to an excess and no improvement of the spalling resistance was found. The amount of aragonite-type calcium carbonate combined is 0.5-5 parts by weight (simply referred to hereinafter as parts) per 100 parts of the refractory aggregate. Too few microcracks develop in the brick and the improvement of the spalling resistance is inadequate when the amount of aragonite-type calcium carbonate combined is less than 0.5 part. On the other hand, the structure becomes porous and the refractory property of the brick declines when it exceeds 5 parts. Although the particle diameter of the aragonite-type calcium carbonate is not particularly

restricted, it is usually about 0.5-10 mm, more preferably 1-3 mm. The development of microcracks tends to decrease when the particle diameter of the aragonite-type calcium carbonate is less than 0.5 mm. Porosity caused by the development of cracks other than microcracks advances and the improvement of the spalling resistance tends to be negated when it exceeds 10 mm. The purity of the aragonite-type calcium carbonate is preferably 80% or more. Low melting-point minerals are produced and the refractory property of the brick declines when this purity is low.

The refractory of the present invention is produced by combining aragonite-type calcium carbonate with the MgO-CaO refractory aggregate, adding known nonaqueous binders such as tar, liquid phenol resin, polyurethane, polypropylene, and wax (usually in a quantity of about 1-5 parts per 100 parts of the refractory aggregate) by the usual method, kneading, molding, and calcining. There is no particular specification as to the process from the addition of the nonaqueous binder up to calcining because it is carried out by the usual methods, but it is preferable to conduct calcining at about 1600-1700°C.

The magnesia-calcia-based refractory of the present invention is useful as a lining refractory for various types of furnaces.

Merits of the invention

The present invention obtains a magnesia-calcia-based refractory with better spalling resistance and thermal impact resistance than known magnesia-calcia-based refractories. The other properties such as the strength of the refractory of the present invention are also as good as or better than those of conventional products.

Practical Examples

The characteristics of the present invention are clarified further below through comparative and practical examples.

Practical Examples 1-3

The raw materials were combined in the proportions (parts) shown in Table 1, 2 parts of polypropylene were added as binder per 100 parts of said composition, kneaded, formed into the usual shape, and calcined at 1650°C.

The particle diameter and such properties of the raw materials in Table 1 were as follows.

I...Natural magnesia clinker, particle diameter 3-1 mm

II...Natural magnesia clinker, particle diameter less than 1 mm

III...Natural dolomite clinker, particle diameter 3-1 mm, MgO = 40%, CaO = 60%

IV...Natural dolomite clinker, particle diameter less than 1 mm, MgO = 40%, CaO = 60%

V...Aragonite-type calcium carbonate, particle diameter 3-1 mm

Table 1.

Raw material	Practical Example		
	1	2	3
I	20	20	20
II	40	40	40
III	30	30	30
IV	10	10	10
V	1	3	5

The refractories obtained were examined by the following methods.

A...Porosity (%): according to JIS R-2205.

B...Bulk specific gravity: according to JIS R-2205.

C...Compression strength (kgf/cm^2): according to JIS R-2206

D...Flexural strength (kgf/cm^2, 1400°C): according to JIS R-2213.

E...Spalling resistance: The refractory was inserted into an electric furnace kept at 1200°C, a cycle of 15 minutes heating, 15 minutes cooling repeated, and the number of cycles until the refractory detached was studied.

The results are shown in Table 2.

Comparative Example 1

A refractory was produced in the same way as in Practical Example 1 except that aragonite-type calcium carbonate was not used.

The results are also shown in Table 2.

Comparative Example 2

A refractory was produced in the same way as in Practical Example 1 except that refined calcite-type calcium carbonate (particle diameter 1 mm or less) was used instead of aragonite-type calcium carbonate.

The results are also shown in Table 2.

Table 2.

Property	Practical Example			Comparative Example	
	1	2	3	1	2
A	16.6	17.5	17.7	16.4	16.8
B	2.91	2.90	2.92	2.89	2.88
C	353	339	310	359	348
D	66	53	48	54	49
E	>15	>15	>15	7	7

It is evident from the results shown in Table 2 that the magnesia-calcia-based refractory of the present invention that combined aragonite-type calcium carbonate had far better spalling resistance and thermal impact resistance in particular than the conventional magnesia-calcia-based refractories that did not combine it.

It is also clear that almost no improvement was found when calcite-type calcium carbonate was used instead of aragonite-type calcium carbonate.